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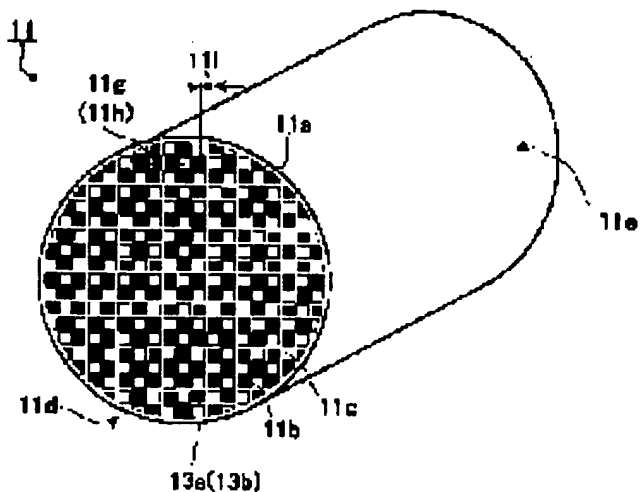
(21)Application number : **2001-037993** (71) **HITACHI METALS LTD**
 (22)Date of filing : **15.02.2001** (72) **OTSUBO YASUHIKO**
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(54) **POROUS CERAMIC HONEYCOMB STRUCTURE**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a honeycomb structure which is not of a complicated structure and is easily manufactured and further captures fine particles contained in an exhaust gas with high efficiency and also cuts a pressure loss to a low level.

SOLUTION: This porous ceramic honeycomb structure comprises an outer peripheral wall and numerous cells surrounded by a cell wall on the inner peripheral side of the outer peripheral wall. Both edge faces of the exhaust gas inflow side and the exhaust gas outflow side of the cells are alternately sealed and the exhaust gas is made to flow into the adjacent cells by allowing the exhaust gas to pass through the pores of the cell wall. Thus fine particles contained in the exhaust gas are captured by the cell wall. In addition, the structure has a section of a square shape surrounded by the cell



wall whose thickness is 0.1 to 0.3 mm, with a cell pitch of 1.4 to 3 mm. Besides the sectional area surrounded by the cell wall is 1.3 mm² or more, or the inside dimension between both internal faces of the cell wall is 1.15 mm or more. Further, the surface of a filter per unit volume is 7 cm²/cm³ or more, preferably 10 cm²/cm³ or more and the porosity of the cell wall is 50 to 70%.

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CLAIMS

[Claim(s)]

[Claim 1] Have the countless cell surrounded with a cell wall by the inner circumference side of a peripheral wall and this peripheral wall, and a both-ends side by the side of exhaust-gas-flow ON of a cell and exhaust-gas-flow appearance is sealed by turns, It is a porosity ceramic honeycomb structured body which catches particles which pass fine pores of a cell wall, pass exhaust gas to an adjacent cell, and are contained in exhaust gas with a cell wall, A section surrounded with a cell wall has quadrangular shape, and, in cell wall thickness, 0.1-0.3 mm and a cell pitch at 1.4-3 mm. A porosity ceramic honeycomb structured body currently making [a cross-section area surrounded with a cell wall] not less than 1.15 mm and a filter surface product per unit volume more than 7 cm²/cm³ for inside dimension between more than 1.3 mm² or a cell wall.

[Claim 2] The porosity ceramic honeycomb structured body according to claim 1 currently making a filter surface product per said unit volume more than 10 cm²/cm³.

[Claim 3] The porosity ceramic honeycomb structured body according to claim 1 or 2 currently making porosity of said cell wall into 50 to 70%.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the porosity ceramic honeycomb structured body which catches the particles in the exhaust gas discharged from a diesel engine, for example.

[0002]

[Description of the Prior Art] In order to call for reduction of the toxic substances contained in the exhaust gas discharged from engines, such as a car, and to respond to this from the preservation side of local environment or earth environment, the catalytic converter for exhaust gas purification is used. One of the catalytic converter of this has a ceramic honeycomb catalyst converter. In order to catch these days the particles contained in the exhaust gas from a diesel power plant, By the porosity ceramic honeycomb structured body (henceforth [a "porosity ceramic honeycomb structured body" is omitted and] a "honeycomb structured body"), the exhaust gas purifying filter which sealed the both-ends side by the side of the exhaust-gas-flow ON of a cell and exhaust-gas-flow appearance by turns has been used.

[0003] Drawing 1 is a perspective view of the honeycomb structured body 11, and drawing 2 is a cross section of the honeycomb structured body 11 of drawing 1. As shown in drawing 1 and drawing 2, the honeycomb structured body 11 is usually approximately cylindrical, It has the countless cell 11c surrounded with the cell wall 11b by the inner circumference side of the peripheral wall 11a and this peripheral wall 11a, and 11 d of inflow side edges of the cell 11c and the both-ends side of the outflow side edge 11e are sealed with the sealing agents 13a and 13b by turns. And the honeycomb structured body 11 grasps the peripheral wall 11a by a gripping member (not shown), is stored in a stowage container (not shown), and is used as the exhaust gas purifying filter. The exhaust gas purifying filter is arranged, for example after the exhaust manifold of a car etc.

[0004] Exhaust gas purification with an exhaust gas purifying filter is performed as follows. By drawing 2, exhaust gas flows from the cell 11c which is carrying out the opening by 11 d of inflow side edges of the honeycomb structured body 11 (10a shows), and after it passes the fine pores (not shown) formed in the cell wall 11b, it is discharged from the outflow side edge 11e (10b shows). And when particles contained in exhaust gas pass to an adjacent cell from the fine pores which continue within the cell wall 11b, they are filtered, and they are caught.

[0005] However, when the quantity of the particles caught increased, and fine pores are got blocked by particles and use for an engine, back pressure increases and an engine output is reduced. For this reason, when the caught particles exceed a constant rate, it is necessary to suppress the increase in back pressure by removing particles. Since particles are the soluble organic components of that it can dissolve in a fixed-carbon-content ingredient and an organic solvent, and an inflammability, if it heats in temperature of not less than about 650 **, they will burn. Then, particles are made to afterburn using heating methods, such as an electric heater, a burner, and a hot wind, and the exhaust gas purifying filter is

reproduced. The method of reproducing particles continuously at low temperature using a catalyst is also taken.

[0006]An important thing is the pressure loss below fixed in the characteristic of this exhaust gas purifying filter, and the time which can continue catching, i.e., catching time, is a long time, suppressing the engine increase in back pressure. If catching time is short, the interval to reproduction becomes short and must enlarge capacity of an exhaust gas purifying filter inevitably.

[0007]On the other hand, conventional technology has the indication of the honeycomb filter which was going to adjust the numerical aperture of the cell by the side of the inflow of exhaust gas, and an outflow, and the cross-section area of the passage direction of a cell, and was going to lessen pressure loss. Namely, in the honeycomb filter of an exhaust gas purifying facility in JP,5-68828,A, Suppose low the pressure loss at the time of exhaust gas passing a filter that exhaust gas can be easily introduced into a cell by setting the cell pitch of each cell which carries out the opening of the numerical aperture by the side of an outflow to the inflow side 20 to 30% as 2.5-5.0 mm, when the numerical aperture by the side of exhaust-gas-flow ON is 60 to 70%. Each cell which carries out an opening to the exhaust-gas-flow ON side has a section hexagon-like centrum, and each cell which carries out an opening to the exhaust-gas-flow appearance side has the statement made into the centrum of section triangular shape in this JP,5-68828,A.

[0008]In another JP,10-57730,A. To a peripheral wall, this peripheral wall, and one, and the breakthrough septum formed in the peripheral wall at honeycomb shape, Two or more breakthroughs divided by the breakthrough septum, and the sealed body formed only in the end part of a breakthrough, Are a ***** ceramic honeycomb filter, and the sealed body is formed in the shape of an approximately checker in the both-ends side of a ceramic honeycomb filter, and. In the cross-section area of the sealed body formation part of a breakthrough, it is smaller than the cross-section area of a sealed body agenesis part, and is making the cross-section area of a sealed body formation part preferably 20% - 50% to the cross-section area of a sealed body agenesis part, and there is a statement to which it is supposed that the pressure loss at the time of the inflow of exhaust gas and an outflow can be reduced.

[0009]The cordierite powder of not less than 30% of porosity is used as aggregate at JP,7-163822,A, To this an ostomy agent, a forming assistant, etc. in the end of cordierite-ized precursor powder In addition, kneading, With the nature ceramics filter of cordierite whose porosity the average pore size of a filter which obtained by performing shaping and calcination is less than [of aggregate / pitch-diameter $\times 0.15^{**}5$ micrometer], and is not less than 30%. There is a statement to which it is supposed that collection efficiency is high, pressure loss is small, and the filter which has the intensity which can be carried [that it is lightweight and compact and] in a car can be provided.

[0010]

[Problem(s) to be Solved by the Invention]However, although a honeycomb filter given in said JP,5-68828,A changes the numerical aperture by the side of exhaust-gas-flow ON and an outflow and is made into the prescribed range, it becomes are an exhaust-gas-flow ON and outflow side, and it is difficult to control a numerical aperture, and complicated [structure]. It becomes complicated [an extrusion public-funds / at the time of fabricating a honeycomb filter raw material / type structure] from a plastic matter to make the inflow side of exhaust gas into the shape of a hexagon, and to make the outflow side into

triangular shape for the section of each cell.

[0011]Although a ceramic honeycomb filter given in JP,10-57730,A changes the cross-section area of the sealed body formation part of a breakthrough, and the cross-section area of a sealed body agenesis part and is made into the prescribed range, it becomes it is difficult to change the cross-section area of a breakthrough and to control, and complicated [structure]. The process of making an extended change of the cross-section area of the sealed body agenesis part of a breakthrough increases.

[0012]Since the nature ceramics filter of cordierite of a statement is using cordierite aggregate of not less than 30% of porosity for JP,7-163822,A, the pore structure consists of fine pores by a cordierite-ized raw material with a big path, and a small chain hole of a path. Therefore, in order to secure the strength property, since 300-2000 micrometers of thickness of a channel septum are required, there is a problem that the differential pressure by the side of an inflow and an outflow becomes large, and pressure loss becomes large.

[0013]By supporting catalysts, such as a platinum metal catalyst, to the cell wall and fine pores of a honeycomb structured body in recent years, the particles in exhaust gas are caught and purifying toxic substances, such as nitrogen oxides contained in exhaust gas, has also been performed. However, since the calorific capacity of a honeycomb structured body becomes large when the thickness of a channel septum is 300-2000 micrometers, time until a catalyst is activated from immediately after engine start becomes long, and the problem that a toxic substance will be discharged in the meantime also has it.

[0014]Therefore, the technical problem of this invention does not have a complicated structure, and is easy to manufacture, and catches the particles contained in exhaust gas efficient, and there is in obtaining the honeycomb structured body which can make pressure loss low. Even if it supports a catalyst, the particles contained in exhaust gas are caught efficient, and it is in obtaining the honeycomb structured body which can make pressure loss low.

[0015]

[Means for Solving the Problem]This invention persons inquired wholeheartedly in view of an aforementioned problem. as a result, a cross-section area which makes quadrangular shape a section surrounded with a cell wall, and is surrounded with cell wall thickness, a cell pitch, and a cell wall or inside dimension between cell walls, and a filter surface product per unit volume -- or, if porosity of a cell wall is chosen further appropriately, Even if structure is not complicated, and manufacture is easy, and particles contained in exhaust gas are caught efficient, and a honeycomb structured body which can make pressure loss low is obtained and also it supports a catalyst, catch particles contained in exhaust gas efficient, and. Knowledge that a honeycomb structured body which can make pressure loss low is obtained was acquired, and it thought out to this invention.

[0016]Namely, a honeycomb structured body of this invention has the countless cell surrounded with a cell wall by the inner circumference side of a peripheral wall and this peripheral wall, and seals a both-ends side by the side of exhaust-gas-flow ON of a cell, and exhaust-gas-flow appearance by turns, It is a porosity ceramic honeycomb structured body which catches particles which pass fine pores of a cell wall, pass exhaust gas to an adjacent cell, and are contained in exhaust gas with a cell wall, A section surrounded with said cell wall has quadrangular shape, and, in cell wall thickness, 0.1-0.3 mm and a cell pitch at 1.4-3 mm. Not less than 1.15 mm and a filter surface product per unit volume are made [a cross-section area surrounded with a cell wall] more than $7 \text{ cm}^2/\text{cm}^3$ for inside dimension

between more than 1.3 mm^2 or a cell wall.

[0017]In this invention, it is preferred to make a filter surface product per said unit volume more than $10 \text{ cm}^2/\text{cm}^3$. In this invention, it is preferred to make porosity of said cell wall into 50 to 70%.

[0018]Next, a reason for composition from this invention is explained.

(Shape of a section surrounded with a cell wall) If a section surrounded with a cell wall is made into quadrangular shape, structure will not be complicated and manufacture will serve as an easy honeycomb structured body. Since an extrusion public-funds type at the time of considering it as a Plastic solid of honeycomb structure from a plastic matter does not have a complicated structure, either, it is easy to manufacture. Quadrangular shape shall also include approximately quadrangular shape from which a length of one side differs about 20%.

[0019](Cell wall thickness) Productivity falls that an extrusion public-funds type plastic matter ejection passage which cell wall thickness uses for considering it as a Plastic solid of honeycomb structure from a plastic matter in less than 0.1 mm is too thin, and a plastic matter is hard to be discharged. On the other hand, if cell wall thickness exceeds 0.3 mm, differential pressure by the side of an inflow and an outflow will become large, and pressure loss will become large. Therefore, cell wall thickness shall be 0.1-0.3 mm.

[0020](Cell pitch) Resistance at the time of exhaust gas going [a cell pitch] into 11 d at less than 1.4 mm in an inflow side of the cell 11c becomes large. On the other hand, since the number of cells per unit sectional area becomes fewer and a filter surface product per unit volume will become small if a cell pitch exceeds 3 mm, it is because pressure loss becomes large. Therefore, a cell pitch shall be 1.4-3 mm.

[0021](A cross-section area surrounded with a cell wall, or inside dimension between cell walls) Resistance at the time of exhaust gas going into 11 d that a cross-section area surrounded with a cell wall is [inside dimension between less than 1.3 mm^2 or a cell wall] less than 1.15 mm by a relation with a filter surface product in an inflow side of the cell 11c becomes large. A cross-section area surrounded with a cell wall shows a cross-section area of a passage direction of one cell.

[0022](Filter surface product per unit volume) A filter surface product means geometric surface area of a cell which exhaust gas passes, and it is expressed with inside dimension $x4/(\text{cell pitch})^2 \times 1/2$ between filter surface product = cell walls per unit volume. In exhaust gas, pressure loss at the time of passage becomes large by relation between a cross-section area surrounded with a cell wall as a filter surface product per unit volume is less than $7 \text{ cm}^2/\text{cm}^3$ in a honeycomb structured body, or inside dimension of a cell wall. Therefore, more than $7 \text{ cm}^2/\text{cm}^3$ make a filter surface product per unit volume preferably more than $10 \text{ cm}^2/\text{cm}^3$ for a filter surface product per unit volume.

[0023](Porosity) In exhaust gas, pressure loss at the time of passage becomes large by a relation with a cross-section area or inside dimension of a cell wall, and a filter surface product per unit volume which are surrounded with a cell wall as porosity of a cell wall is less than 50%. Support of a catalyst becomes difficult in supporting catalysts, such as a platinum metal catalyst, to a cell wall or fine pores. On the other hand, if porosity exceeds 70%, collection efficiency of that intensity falls and particles will fall. Therefore, porosity is made into 50 to 70%. Porosity is measured using a mercury pressure ON type porosimeter.

[0024]

[Embodiment of the Invention]Hereafter, an embodiment of the invention is described in

detail.

[0025]The honeycomb structured body 11 shown in drawing 1 and drawing 2 was produced as follows.

(Adjustment of basic-raw-materials powder) Measure powder, such as kaolin, talc, silica, hydroxylation aluminum, and alumina, and chemical composition with a mass ratio. SiO_2 :47-53%, $\text{aluminum}_2\text{O}_3$:32-38%, MgO : The nature ceramics raw material powder of cordierite used as 12 to 16% was adjusted. As for this ceramics raw material powder, below 2.5 mass % contains ingredient [which is mixed in others unescapable], for example, CaO , Na_2O , K_2O , TiO_2 , Fe_2O_3 , PbO , and P_2O_5 as a whole.

[0026]To (addition of a forming assistant and an ostomy agent and refining of a plastic matter), next the precursor powder end of these nature ceramics of cordierite, as a forming assistant as methyl cellulose, hydroxypropylmethylcellulose, and an ostomy agent, Graphite, wheat flour, starch, etc. were selected suitably, and it added, and mixed enough by dry type. Subsequently, the water of the stipulated amount was poured in, still more sufficient mixing was performed, and the plastic matter in which extrusion molding is possible was produced.

[0027](Extrusion molding) Next, extrusion molding was carried out using the extrusion-molding public-funds type of a general structure. In drawing 3, the part drawing of the Plastic solid in which (a) has honeycomb structure, and (b) are extrusion-molding public-funds type important section sectional views. The numerals parenthesized by drawing 3 (a) show the part of the honeycomb structured body 11 after calcination. In order that extrusion-molding public-funds type 20 may gather a plastic matter from many supply paths 21a and these supply paths 21a and they may form in specified shape the die 21 with the ejection passage 21b formed in the shape of a lattice, and the peripheral wall 11a of the honeycomb structured body 11 by drawing 3, The discharge of the masking plate 22 and plastic matter which adjust plastic matter inflow is adjusted, and it consists of the presser-foot frame 23 etc. which adjust the peripheral wall 11a of the honeycomb structured body 11. The bottom to a top is the direction of extrusion (an arrow shows), and extrusion-molding public-funds type 20 has extruded the plastic matter from the supply path 21a to the ejection passage 21b. And the section surrounded with a cell wall produced the Plastic solid which has quadrangular shape, into which the cross-section area of 11g surrounded with 11 t of cell wall thickness, the cell pitch 11i, and a cell wall and the inside dimension of 11 h between cell walls, and the filter surface product per unit volume were changed and which has honeycomb structure by extrusion-molding public-funds type 20.

[0028](Calcination) Next, the Plastic solid which has this honeycomb structure was calcinated using the batch type firing furnace. In 150 mm and length, the porosity of 150 mm and the cell wall 11b after calcination at 60%. [the outer diameter of the peripheral wall 11a] The section surrounded with the cell wall 11b has quadrangular shape, and as shown in Table 1, the honeycomb structured body 11 which changed the cross-section area of 11g surrounded with 11 t of cell wall thickness, the cell pitch 11i, and a cell wall or the inside dimension 11i between cell walls, and the filter surface product per unit volume was obtained.

[0029](Sealing) Next, the cell 11c of 11 d of inflow side edges of a baking body which have honeycomb structure was sealed with the sealing agent 13a every piece, and it sealed with

the sealing agent 13b in the exhaust-gas-flow appearance side edge 11e only about the cell 11c which is not sealed by 11 d of inflow side edges. The sealing agents 13a and 13b used the nature ceramics of cordierite.

[0030]Next, air was flowed into each honeycomb structured body 11 as flow [of 7.5 Nm] ³/min, the inflow side measured the differential pressure (mmAq) by the side of [11e] 11 d and an outflow, and pressure loss test equipment (not shown) estimated the pressure loss of each honeycomb structured body 11. Evaluation of pressure loss performed that in which differential pressure exceeds [less than 250 mmAq] right (O) and 350mmAq for A (O) and 250 - 350mmAq as NG (x). The result is summarized in Table 1 and shown.

[0031]

(Table 1)

Classification cell wall thickness cell pitch cross-section area Inside dimension filter surface product . Differential pressure Example 1 of an evaluation invention of pressure loss (mm), (mm) (mm²), and (mm) (cm²/cm³) (mmAq) 0.30 1.80 2.25 1.50 9.3 Example 2 of a 266 O invention 0.30 1.47.1.37 1.17 10.8 The example 3 of a 249 O invention. 0.25 1.47 1.49 1.22. 11.3 Example 4 of a 238 O invention 0.23. 1.51 1.64 1.31 11.0. 233 O comparative example 1 0.432.54 4.45. 2.11 6.5 414 x comparative example 2 0.15. 1.27 1.25 1.12 13.9. 452 x comparative example 3 0.30 3.00 7.29 2.70 6.0 368 x comparative example 4 0.30 1.27 0.94 0.97 12.0 425 x comparative example 5 0.30 3.50 10.24 3.20 5.2 In the 371 x (notes) table 1. Inside dimension omits the inside dimension of 11 h between cell walls, a filter surface product omits the filter surface product per unit volume, respectively, and the cross-section area of 11 g by which a cross-section area is surrounded with a cell wall is shown.

[0032]From Table 1, the cell wall thickness 11c the examples 1-4 of an invention 0.1-0.3 mm, In the cross-section area of 11 g by which the cell pitch 11i is surrounded with 1.4-3 mm and a cell wall, the inside dimension of 11 h between more than 1.3 mm² or a cell wall Not less than 1.15 mm, It turns out that the filter surface product per unit volume serves as 7cm²/cm³, and the honeycomb structured body 11 that has small differential pressure, and little [since it is 10 cm² / more than cm³ preferably] pressure loss.

[0033]On the other hand, although the inside dimension 11i between more than 1.3 mm² or a cell wall is not less than 1.15 mm, the cross-section area of 11 g surrounded with a cell wall the comparative example 1, Since cell wall thickness is over 0.3 mm, the filter surface product per unit volume is less than 7 cm²/cm³, and it turns out that differential pressure is large and pressure loss is large. Although the filter surface products per unit volume are 7 cm² / more than cm³, the comparative examples 2 and 4, The cross-section area of 11 g surrounded with a cell wall is [the inside dimension of 11 h between less than 1.3 mm² or a cell wall] less than 1.15 mm, and the cell pitch 11i is less than 1.4, and it turns out that differential pressure is large and pressure loss is large. The filter surface product per unit volume is less than 7 cm²/cm³, and the comparative example 3 is understood that differential pressure is large and pressure loss is large, although the cross-section area of 11 g surrounded with a cell wall is [the inside dimension 11i between more than 1.3 mm² or a cell wall] not less than 1.15 mm. Although the inside dimension 11i between more than 1.3 mm² or a cell wall is not less than 1.15 mm, the cross-section area of 11 g surrounded with a cell wall the comparative example 5, A cell pitch exceeds 3 mm, and since the filter surface product per unit volume is less than 7 cm²/cm³, it turns out that

differential pressure is large and pressure loss is large.

[0034](Catalyst support) The honeycomb structured body 11 of the examples 1-4 of an invention supports a catalyst in the cell wall 11b and fine pores if needed. When a platinum metal catalyst is supported to the honeycomb structured body 11, From the caught carbon burning at low temperature continuously by a chemical reaction with NO_2 formed of the catalytic reaction of NO_x in an exhaust gas component. Combustion temperature can be reproduced continuously, without carrying out the erosion of the honeycomb structured body by making it fall compared with the case where it is made to burn by electric heater, a burner, etc.

[0035]

[Effect of the Invention]Above, according to the honeycomb structured body of this invention as explanation in details, the particles which it becomes structure is not complicated and easy to manufacture, and are contained in exhaust gas are caught efficient, and pressure loss can be made low.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]It is a perspective view of a honeycomb structured body.

[Drawing 2]It is a cross section of an example of the exhaust gas purifying filter 10 using the honeycomb structured body of drawing 1.

[Drawing 3]The partial part of the Plastic solid in which (a) has honeycomb structure, and (b) are extrusion-molding public-funds type important section sectional views.

[Description of Notations]

10a: Inflow

10b: Outflow

11: Honeycomb structured body

11a: Peripheral wall

11b: Cell wall

11c: Cell

11d: Inflow side edge

11e: Outflow side edge
 11f: Inflow side edge
 11g: The cross-section area surrounded with a cell wall
 11h: Inside dimension between cell walls
 11i: Cell pitch
 11t: Cell wall thickness
 13a, 13b: Sealing agent
 20: Extrusion-molding public-funds type
 21: Die
 21a: Supply path
 21b: Ejection passage
 22: Masking plate
 23: Presser-foot frame

[Translation done.]

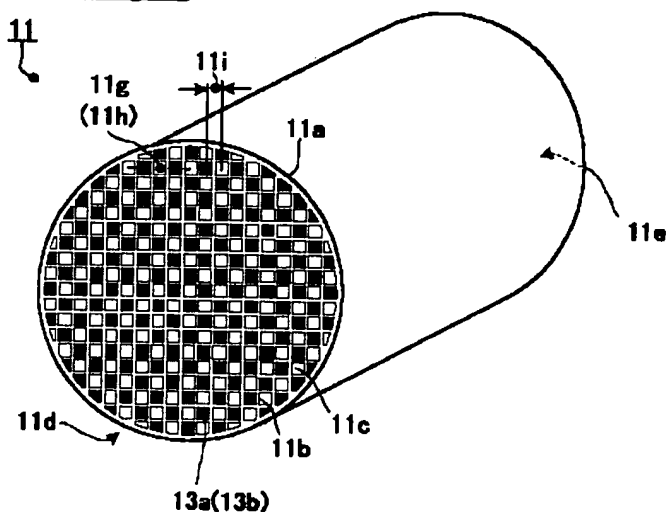
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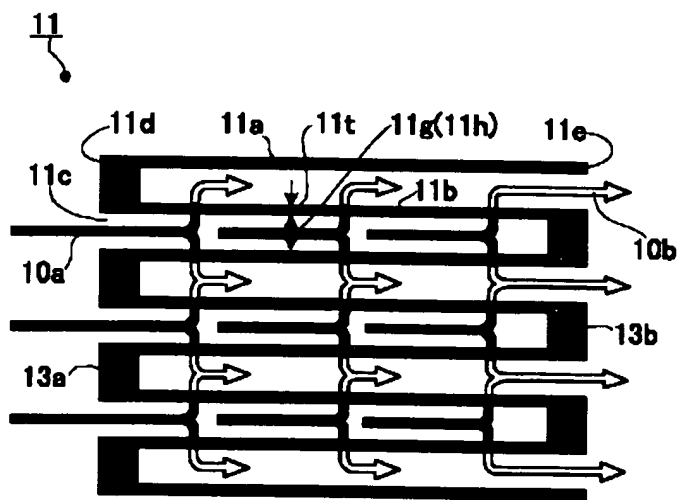
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DRAWINGS

[Drawing 1]

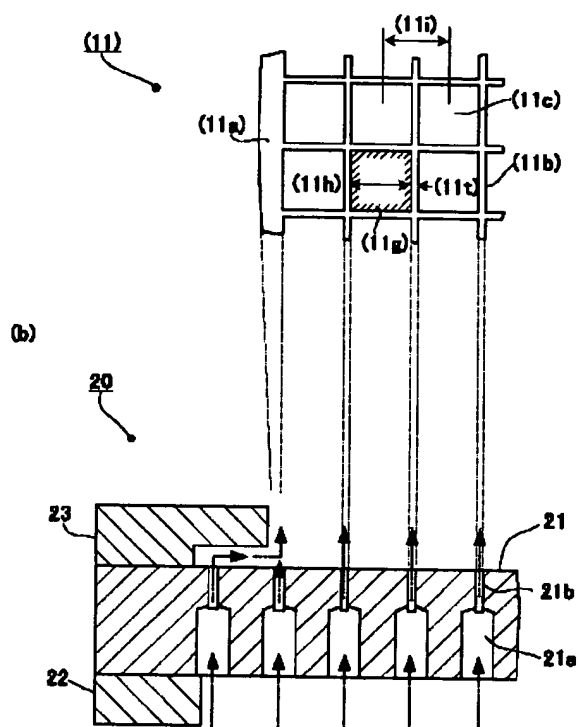


[Drawing 2]



[Drawing 3]

(a)



[Translation done.]

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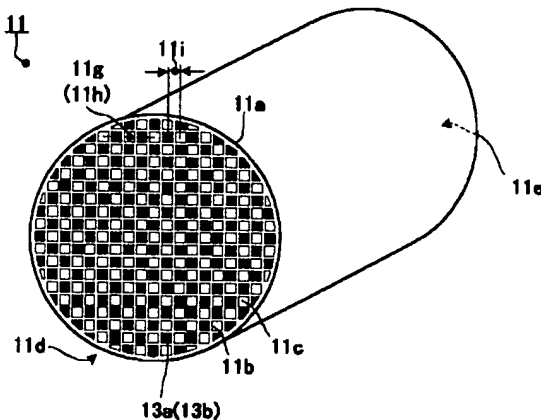
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(54) 【発明の名称】 多孔質セラミックハニカム構造体

(57) 【要約】

【課題】 構造が複雑でなく、製造が容易で、且つ、排気ガスに含まれる微粒子を高効率に捕集すると共に圧力損失を低くできるハニカム構造体を得る。

【解決手段】 外周壁と、この外周壁の内周側でセル壁により囲まれた無数のセルを有し、セルの排気ガス流入側及び排気ガス流出側の両端面を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する多孔質セラミックハニカム構造体であって、セル壁で囲まれる断面が四角形状を有し、セル壁厚が0.1~0.3mm、セルピッチが1.4~3mmで、セル壁で囲まれる断面積を1.3mm²以上又はセル壁間の内寸を1.15mm以上、単位体積あたりのフィルタ表面積を7cm²/cm³以上、好ましくは単位体積あたりのフィルタ表面積を10cm²/cm³以上、セル壁の気孔率を50~70%とする。



【特許請求の範囲】

【請求項1】 外周壁と、この外周壁の内周側でセル壁により囲まれた無数のセルを有し、セルの排気ガス流入側及び排気ガス流出側の両端面を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する多孔質セラミックハニカム構造体であって、セル壁で囲まれる断面が四角形状を有し、セル壁厚が0.1～0.3mm、セルピッチが1.4～3mmで、セル壁で囲まれる断面積を1.3mm²以上又はセル壁間の内寸を1.15mm以上、単位体積あたりのフィルタ表面積を7cm²/cm³以上としていることを特徴とする多孔質セラミックハニカム構造体。

【請求項2】 前記単位体積あたりのフィルタ表面積を10cm²/cm³以上としていることを特徴とする請求項1に記載の多孔質セラミックハニカム構造体。

【請求項3】 前記セル壁の気孔率を50～70%としていることを特徴とする請求項1又は請求項2に記載の多孔質セラミックハニカム構造体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、例えば、ディーゼルエンジンから排出される排気ガス中の微粒子を捕集する多孔質セラミックハニカム構造体に関する。

【0002】

【従来技術】地域環境や地球環境の保全面から、自動車などのエンジンから排出される排気ガスに含まれる有害物質の削減が求められ、これに応えるため排気ガス浄化用の触媒コンバータが用いられている。この触媒コンバータのひとつにセラミックハニカム触媒コンバータがある。また、最近ではディーゼルエンジンからの排気ガス中に含まれる微粒子を捕集するために、多孔質セラミックハニカム構造体（以下、「多孔質セラミックハニカム構造体」を略して「ハニカム構造体」という）で、セルの排気ガス流入側及び排気ガス流出側の両端面を交互に目封じした排気ガス浄化フィルタが使用されてきている。

【0003】図1はハニカム構造体11の斜視図であり、図2は、図1のハニカム構造体11の断面模式図である。図1及び図2に示すように、通常、ハニカム構造体11は略円筒状で、外周壁11aと、この外周壁11aの内周側でセル壁11bにより囲まれた無数のセル11cを有し、セル11cの流入側端面11d、流出側端面11eの両端面を交互に封止材13a、13bで目封じされている。そしてハニカム構造体11は、その外周壁11aを把持部材（図示せず）で把持して収納容器（図示せず）内に収納され排気ガス浄化フィルタとして用いられる。また排気ガス浄化フィルタは、例えば自動車の排気マニホルドの後などに配置されている。

【0004】排気ガス浄化フィルタでの排気ガス浄化は、以下の通り行われる。図2で、排気ガスは、ハニカ

ム構造体11の流入側端面11dで開口しているセル11cから流入（10aで示す）し、セル壁11bに形成された細孔（図示せず）を通過した後、流出側端面11eから排出（10bで示す）される。そして、排気ガス中に含まれる微粒子などは、セル壁11b内で連続する細孔から隣接セルに通過する際に濾過され、捕集される。

【0005】しかし、捕集される微粒子の量が多くなると細孔が微粒子によって詰まり、エンジンに用いた場合に背圧が増加してエンジン出力を低下させる。このため、捕集された微粒子が一定量を超えたときに微粒子を除去することで背圧増加を抑える必要がある。微粒子は、固定炭素成分と有機溶剤に溶解可能で可燃性の可溶性有機成分であるので、約650℃以上の温度に加熱すれば燃焼する。そこで、電気ヒータ、バーナ、熱風などの加熱手段を用いて微粒子を再燃焼させて、排気ガス浄化フィルタを再生している。又、触媒を使用して低温で連続的に微粒子を再生する方法もとられている。

【0006】この排気ガス浄化フィルタの特性で重要なことは、一定以下の圧力損失で、エンジンの背圧増加を抑えつつ捕集が継続できる時間、即ち捕集時間が長いことである。捕集時間が短いと再生までのインターバルが短くなり、必然的に排気ガス浄化フィルタの容積を大きくしなければならなくなる。

【0007】これに対して従来技術には、排気ガスの流入側と流出側のセルの開口率やセルの流路方向の断面積を調整して圧力損失を少なくしようとしたハニカムフィルタの開示がある。即ち、特開平5-68828号公報には、排気ガス浄化装置のハニカムフィルタにおいて、排気ガス流入側の開口率が60～70%のとき流出側の開口率を20～30%、流入側に開口する各セルのセルピッチを2.5～5.0mmに設定することで、排気ガスがフィルタを通過する際の圧力損失を低く、またセル中に排気ガスを容易に導入できるとしている。また、この特開平5-68828号公報には、排気ガス流入側に開口する各セルは断面六角形状の中空部を有すると共に、排気ガス流出側に開口する各セルは断面三角形の中空部とする記載がある。

【0008】また別の特開平10-57730号公報には、外周壁と、この外周壁と一体にかつ外周壁内にハニカム状に形成された貫通孔隔壁と、貫通孔隔壁により仕切られた複数の貫通孔と、貫通孔の一端部のみに形成された封止体と、を備えたセラミックハニカムフィルタであって、封止体はセラミックハニカムフィルタの両端面において略市松模様状に形成されていると共に、貫通孔の封止体形成部の断面積を、封止体非形成部の断面積よりも小さく、好ましくは封止体形成部の断面積を封止体非形成部の断面積に対し20%～50%にすることで、排ガスの流入時及び流出時における圧力損失を低減できるとする記載がある。

【0009】また、特開平7-163822号公報には、気孔率30%以上のコーゼライト粉末を骨材とし、これにコーゼライト化原料粉末、造孔剤、成形助剤等を加えて、混練、成形、焼成を行って得た、フィルタの平均細孔径が骨材の平均径 $\times 0.15 \pm 5 \mu\text{m}$ 以内、気孔率が30%以上であるコーゼライト質セラミックフィルタによって、捕集効率が高く、圧力損失が小さく、軽量且つコンパクトで自動車に搭載可能な強度を有するフィルタが提供できるとする記載がある。

【0010】

【発明が解決しようとする課題】しかしながら、前記特開平5-68828号公報に記載のハニカムフィルタは、排気ガス流入側と流出側の開口率を異ならせて所定範囲としているが、排気ガス流入側と流出側で開口率を制御することは難しく、構造も複雑となる。また、各セルの断面を、排気ガスの流入側を六角形状、流出側を三角形状とするのは、坏土からハニカムフィルタ素材を成形する際の押出用金型の構造も複雑となる。

【0011】また、特開平10-57730号公報に記載のセラミックハニカムフィルタは、貫通孔の封止体形成部の断面積と封止体非形成部の断面積を異ならせて所定範囲としているが、貫通孔の断面積を異ならせ制御することは難しく、構造も複雑となる。また、貫通孔の封止体非形成部の断面積を拡張変更する工程が増加する。

【0012】特開平7-163822号公報に記載のコーゼライト質セラミックフィルタは、気孔率30%以上のコーゼライト骨材を使用していることから、その細孔構造は径の大きなコーゼライト化原料による細孔と、径の小さな連鎖孔からなる。そのため、その強度特性を確保するために、流路隔壁の厚さが300~2000 μm 必要なため、流入側と流出側の差圧が大きくなり、圧力損失が大きくなるという問題がある。

【0013】また近年、ハニカム構造体のセル壁や細孔に白金族金属触媒などの触媒を担持することで、排気ガス中の微粒子を捕集すると共に、排気ガスに含まれる窒素酸化物など有害物質を浄化することも行われてきている。しかし、流路隔壁の厚さが300~2000 μm ある場合は、ハニカム構造体の熱容量が大きくなるため、エンジン始動直後から触媒が活性化されるまでの時間が長くなり、その間、有害物質が排出されてしまうという問題もある。

【0014】従って、本発明の課題は、構造が複雑でなく、製造が容易で、且つ、排気ガスに含まれる微粒子を高効率に捕集すると共に、圧力損失を低くできるハニカム構造体を得ることにある。更に、触媒を担持しても、排気ガスに含まれる微粒子を高効率に捕集すると共に圧力損失を低くできるハニカム構造体を得ることにある。

【0015】

【課題を解決するための手段】本発明者らは、上記課題に鑑み鋭意研究した。その結果、セル壁で囲まれる断面

を四角形状とし、セル壁厚、セルピッチ、セル壁で囲まれる断面積又はセル壁間の内寸、単位体積あたりのフィルタ表面積、又は更にセル壁の気孔率を適切に選択すれば、構造が複雑でなく、製造が容易で、且つ、排気ガスに含まれる微粒子を高効率に捕集すると共に圧力損失を低くできるハニカム構造体を得られ、更に触媒を担持しても、排気ガスに含まれる微粒子を高効率に捕集すると共に、圧力損失を低くできるハニカム構造体を得られるとの知見を得、本発明に想到した。

10 【0016】即ち、本発明のハニカム構造体は、外周壁と、この外周壁の内周側でセル壁により囲まれた無数のセルを有し、セルの排気ガス流入側及び排気ガス流出側の両端面を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する多孔質セラミックハニカム構造体であって、前記セル壁で囲まれる断面が四角形状を有し、セル壁厚が0.1~0.3mm、セルピッチが1.4~3mmで、セル壁で囲まれる断面積を1.3mm²以上又はセル壁間の内寸を1.15mm以上、単位体積あたりのフィルタ表面積を7cm²/cm³以上としていることを特徴とする。

20 【0017】本発明においては、前記単位体積あたりのフィルタ表面積を10cm²/cm³以上としていることが好ましい。更に、本発明においては、前記セル壁の気孔率を50~70%としていることが好ましい。

【0018】次に、本発明での構成の理由を説明する。

（セル壁で囲まれる断面の形状）セル壁で囲まれる断面を四角形状とすれば、構造が複雑でなく、製造が容易なハニカム構造体となる。また坏土からハニカム構造の成形体とする際の押出用金型も、構造が複雑でないため製作が容易である。なお、四角形状は一辺の長さが20%近く異なる略四角形状も含むものとする。

30 【0019】（セル壁厚）セル壁厚が0.1mm未満では、坏土からハニカム構造の成形体とするのに用いる押出用金型の坏土排出通路が細すぎて坏土が排出されにくく生産性が低下する。一方、セル壁厚が0.3mmを超えると、流入側と流出側の差圧が大きくなり、圧力損失が大きくなる。従って、セル壁厚を0.1~0.3mmとする。

40 【0020】（セルピッチ）セルピッチが1.4mm未満では、排気ガスがセル11cの流入側11dに入る際の抵抗が大きくなる。一方、セルピッチが3mmを超えると、単位断面積あたりのセル数が減ることから単位体積あたりのフィルタ表面積が小さくなるため、圧力損失が大きくなるためである。従って、セルピッチを1.4~3mmとする。

50 【0021】（セル壁で囲まれる断面積又はセル壁間の内寸）セル壁で囲まれる断面積が1.3mm²未満又はセル壁間の内寸が1.15mm未満であると、フィルタ表面積との関係で排気ガスがセル11cの流入側11d

に入る際の抵抗が大きくなる。なお、セル壁で囲まれる断面積は、一つのセルの流路方向の断面積を示す。

【0022】(単位体積あたりのフィルタ表面積) フィルタ表面積とは、排気ガスが通過するセルの幾何学的表面積をいい、

単位体積あたりのフィルタ表面積=セル壁間の内寸×4÷(セルピッチ)²×1/2

で表される。ハニカム構造体において単位体積あたりのフィルタ表面積が7cm²/cm³未満であると、セル壁で囲まれる断面積又はセル壁の内寸との関係で排気ガスが通過時の圧力損失が大きくなる。従って、単位体積あたりのフィルタ表面積を7cm²/cm³以上、好ましくは、単位体積あたりのフィルタ表面積を10cm²/cm³以上とする。

【0023】(気孔率)セル壁の気孔率が50%未満であると、セル壁で囲まれる断面積又はセル壁の内寸、単位体積あたりのフィルタ表面積との関係で排気ガスが通過時の圧力損失が大きくなる。また、セル壁や細孔に白金族金属触媒など触媒を担持する場合には触媒の担持が難しくなる。一方、気孔率が70%を超えると、強度が低下するのと微粒子の捕集効率が低下する。従って、気孔率は50~70%とする。なお気孔率は、水銀圧入式ポロシメータを用いて測定する。

【0024】

【発明の実施の形態】以下、発明の実施の形態を詳細に説明する。

【0025】図1及び図2に示すハニカム構造体11を以下のようにして作製した。

(基本原料粉末の調整)カオリン、タルク、シリカ、水酸化アルミ、アルミナなどの粉末を計量して、化学組成が質量比で、SiO₂:47~53%、Al₂O₃:32~38%、MgO:12~16%となるコーディエライト質セラミックス原料粉末を調整した。該セラミックス原料粉末は他に不可避免的に混入する成分例えば、CaO、Na₂O、K₂O、TiO₂、Fe₂O₃、PbO、P₂O₅を全体として2.5質量%以下含んでいる。

【0026】(成形助剤及び造孔剤の添加と、坏土の精製)次に、このコーディエライト質セラミックの原料粉末に対し、成形助剤としてメチルセルロースとヒドロキシプロピルメチルセルロース、造孔剤として、グラファイト、小麦粉、でん粉などを適宜選定して添加し、乾式で十分混合した。次いで、規定量の水を注入して更に十分な混合を行い、押出成形可能な坏土を作製した。 *

(表1)

区分	セル壁厚 (mm)	セルピッチ (mm)	断面積 (mm ²)	内寸 (mm)	フィルタ表面積 (cm ² /cm ³)	差圧 (mmAq)	圧力損失 の評価
発明例1	0.30	1.80	2.25	1.50	9.3	266	○
発明例2	0.30	1.47	1.37	1.17	10.8	249	◎
発明例3	0.25	1.47	1.49	1.22	11.3	238	◎
発明例4	0.23	1.51	1.64	1.31	11.0	233	◎

*【0027】(押出成形)次に、一般的な構造の押出成形用金型を用い押出成形した。図3で、(a)はハニカム構造を有する成形体の部分図、(b)は押出成形用金型の要部断面図である。なお、図3(a)で括弧した符号は焼成後のハニカム構造体11の部位を示す。図3で、押出成形用金型20は、多数の供給通路21aとこの供給通路21aから坏土を集合すると共に格子状に形成する排出通路21bを持つダイ21と、ハニカム構造体11の外周壁11aを所定形状に形成するために、坏土流入量の調整をするマスキングプレート22、坏土の排出量の調節をすると共にハニカム構造体11の外周壁11aの調節を行う押さえ棒23などからなる。なお、押出成形用金型20は、下から上が押出方向(矢印で示す)であり、坏土を供給通路21aから排出通路21bに押し出している。そして、押出成形用金型20で、セル壁で囲まれる断面が四角形状を有し、セル壁厚11t、セルピッチ11i、セル壁で囲まれる断面積11g及びセル壁間の内寸11h、単位体積あたりのフィルタ表面積を変えた、ハニカム構造を有する成形体を作製した。

【0028】(焼成)次に、このハニカム構造を有する成形体を、バッチ式焼成炉を用いて焼成を行った。焼成後、外周壁11aの外径が150mm、長さが150mm、セル壁11bの気孔率が60%で、セル壁11bで囲まれる断面が四角形状を有し、表1に示すように、セル壁厚11t、セルピッチ11i、セル壁で囲まれる断面積11g又はセル壁間の内寸11i、単位体積あたりのフィルタ表面積を変えたハニカム構造体11を得た。

【0029】(目封じ)次に、ハニカム構造を有する焼成体の流入側端面11dのセル11cを一個おきに封止材13aで目封じし、排気ガス流出側端面11eでは流入側端面11dで目封じしてないセル11cについてのみ封止材13bで目封じした。なお、封止材13a、13bはコーディエライト質セラミックを用いた。

【0030】次に、圧力損失試験装置(図示せず)で、各ハニカム構造体11に流量7.5Nm³/minとして空気を流入し、流入側11dと流出側11eの差圧(mmAq)を測定し、各ハニカム構造体11の圧力損失を評価した。なお、圧力損失の評価は、差圧が250mmAq未満を優(◎)、250~350mmAqを良(○)、350mmAqを超えるものをNG(×)として行った。その結果を表1に纏めて示す。

【0031】

7							8
比較例1	0.43	2.54	4.45	2.11	6.5	414	×
比較例2	0.15	1.27	1.25	1.12	13.9	452	×
比較例3	0.30	3.00	7.29	2.70	6.0	368	×
比較例4	0.30	1.27	0.94	0.97	12.0	425	×
比較例5	0.30	3.50	10.24	3.20	5.2	371	×

(注) 表1で、断面積はセル壁で囲まれる断面積11gを、内寸はセル壁間の内寸11hを、フィルタ表面積は単位体積あたりのフィルタ表面積をそれぞれ略して示す。

【0032】表1から、発明例1～4は、セル壁厚11cが0.1～0.3mm、またセルピッチ11iが1.4～3mm、セル壁で囲まれる断面積11gが1.3mm²以上又はセル壁間の内寸11hが1.15mm以上、単位体積あたりのフィルタ表面積が7cm²/cm³、好ましくは10cm²/cm³以上であるので、差圧が小さくて圧力損失の少ないハニカム構造体11となっていることがわかる。

【0033】一方、比較例1は、セル壁で囲まれる断面積11gが1.3mm²以上又はセル壁間の内寸11iが1.15mm以上であるが、セル壁厚が0.3mmを越えているため、単位体積あたりのフィルタ表面積が7cm²/cm³未満であり、差圧が大きく、圧力損失が大きいことがわかる。比較例2、4は、単位体積あたりのフィルタ表面積が7cm²/cm³以上ではあるが、セル壁で囲まれる断面積11gが1.3mm²未満又はセル壁間の内寸11hが1.15mm未満であり、またセルピッチ11iが1.4未満であり、差圧が大きく、圧力損失が大きいことがわかる。比較例3は、セル壁で囲まれる断面積11gが1.3mm²以上又はセル壁間の内寸11iが1.15mm以上であるが、単位体積あたりのフィルタ表面積が7cm²/cm³未満であり、差圧が

大きく、圧力損失が大きいことがわかる。比較例5は、セル壁で囲まれる断面積11gが1.3mm²以上又はセル壁間の内寸11iが1.15mm以上であるが、セルピッチが3mmを超え、単位体積あたりのフィルタ表面積が7cm²/cm³未満であるので、差圧が大きく、圧力損失が大きいことがわかる。

【0034】(触媒担持) 発明例1～4のハニカム構造体11は、必要に応じて、セル壁11b及び細孔内に触媒を担持する。ハニカム構造体11に白金族金属触媒を担持した場合には、捕集したカーボンが排気ガス成分中のNO_xの触媒反応によって形成されるNO₂との化学反応により連続的に低温で燃焼されることから、燃焼温度は電気ヒーターやバーナなどで燃焼させる場合に比べ

低下させることでハニカム構造体を溶損させることなく、連続的に再生することが出来る。

【0035】

【発明の効果】以上詳細に説明のとおり、本発明のハニカム構造体によれば、構造が複雑でなく、製造が容易となり、且つ、排気ガスに含まれる微粒子を高効率に捕集すると共に圧力損失を低くできる。

【図面の簡単な説明】

【図1】ハニカム構造体の斜視図である。

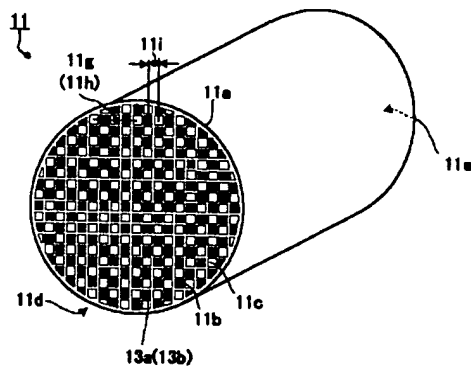
【図2】図1のハニカム構造体を用いた排気ガス浄化フィルタ10の一例の断面模式図である。

【図3】(a)はハニカム構造を有する成形体の部分部、(b)は押出成形用金型の要部断面図である。

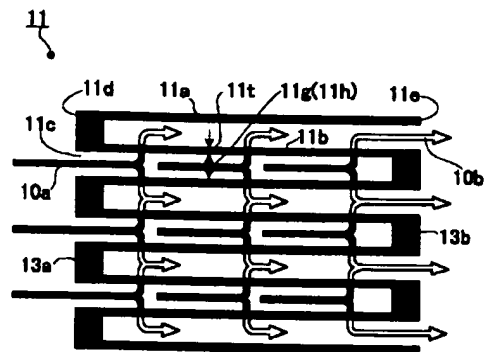
【符号の説明】

10a：流入
10b：流出
11：ハニカム構造体
11a：外周壁
11b：セル壁
11c：セル
11d：流入側端面
11e：流出側端面
11f：流入側端面
11g：セル壁で囲まれる断面積
11h：セル壁間の内寸
11i：セルピッチ
11t：セル壁厚
13a、13b：封止材
20：押出成形用金型
21：ダイ
21a：供給通路
21b：排出通路
22：マス킹プレート
23：押さえ枠

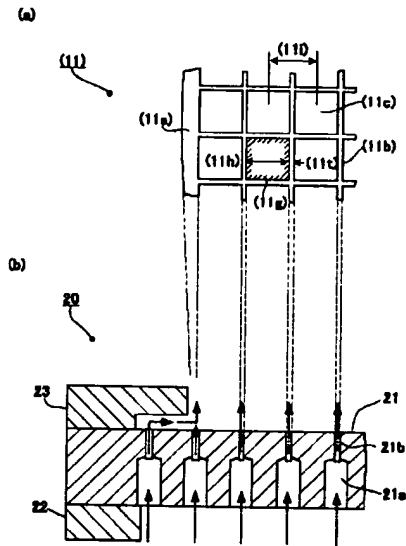
【図1】



【図2】



【図3】



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